

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>C23C 18/20</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 90/00634</b> <b>(43) International Publication Date:</b> <b>25 January 1990 (25.01.90)</b>
<b>(21) International Application Number:</b> PCT/US89/02795 <b>(22) International Filing Date:</b> 29 June 1989 (29.06.89)  <b>(30) Priority data:</b> 216,406 7 July 1988 (07.07.88) US 351,962 17 May 1989 (17.05.89) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor:</b> BURCH, Robert, Ray ; 611 Brecknock Drive, Ex-ton, PA 19341 (US).  <b>(74) Agent:</b> MAYER, Nancy, S.; E.I. du Pont de Nemours and Company, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> METALLIZED POLYMERS AND METHOD  <b>(57) Abstract</b>  A method is disclosed for metallizing polymers comprising generating anionic sites on the structures, contacting same with the cation of the metal and then reducing the metal cation to metal at the anionic sites or treating the metal cations to form a semiconductor. The metallized polymers are useful as electrical conductors or semiconductors.		

Best Available Copy

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

TITLE

## METALLIZED POLYMERS AND METHOD

5        CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of copending application Serial No. 07/216,406 filed on July 7, 1988.

BACKGROUND OF THE INVENTION

10        This invention relates to metallizing polymer structures in the form of films, fibers and other geometric shapes. The metallized polymer structures of the present invention are characterized in that metal uniformly penetrates into the polymer matrix.

15        In the process for their preparation, metal cations are electrostatically bonded to the polymer, and then reduced to the metallic state. The reaction of metal cation with a semiconductor-forming compound likewise results in a semiconductor imbided polymer.

20        U.S. 4,634,805 discloses conductive cable and woven polymer fabric in which the individual filaments are coated with an adherent metal. The method for accomplishing the coating operation requires substrate activation with palladium chloride

25        and/or tin chloride.

German Application No. 2,820,502 discloses a process for metallizing polyamides by placing the polymer in an acidic colloidal palladium solution containing an excess of stannous ions. This

30        activated material is then treated with an acid or a base and is subsequently coated with metal at room temperature by a currentless method using a basic metallic salt solution.

German Application No. 3,139,313 discloses

35        polymer fibers metallized by a currentless method after palladium chloride surface activation.

Jones, et al., Materials Letters, Vol. 2, Number 5B, 462 to 467 (1984) discloses a hybrid cable  
5 consisting of a bundle of synthetic fibers coated with a thin metallic layer.

U.S. 4,374,893 discloses polyamides with permanent conducting properties having on the surface a layer of copper sulfide with an atomic ratio of  
10 Cu/S of 1.5 to 2. Such polyamides are metallized by treating with hydrogen sulfide under pressure, followed by an aqueous solution of a copper salt, optionally in the presence of a swelling agent and a reducing agent. If no reducing agent is present in  
15 the copper salt solution, an after-treatment is carried out in the presence of a reducing agent.

U.S. Patent 4,785,038 discloses a solvent system of liquid sulfoxide, a base and an alcohol or water for dissolving aromatic polyamides, .  
20 polybenzimidazoles and polyureas which are known to be difficult to dissolve.

#### SUMMARY OF THE INVENTION

This invention concerns metallized polymers and a method for their production. The polymer can be a  
25 single polymer or a copolymer or composite. For the sake of brevity, the term "polymers" will be employed herein to designate all of such polymers in whatever geometric form they appear. The term "metal" will be employed to designate the coating or imbibing  
30 materials, it being understood that the term encompasses pure metals, including mixtures of metals, as well as metal-containing substances comprising other moieties as well, for instance, metal-containing semiconductors. The term  
35 "metallized" as used herein describes polymers which are metal coated, metal imbibed, or semiconductor

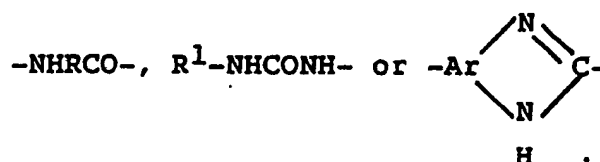
imbibed. The imbibed polymers contain metal which has uniformly penetrated into the polymer matrix.

5 The geometry of the polymer substrate before metallization, and of the metallized substrate, can vary, and will not influence the subject or method of this invention. Representative shapes include fibers and films.

10 One type of metallized polymer of this invention comprises a polymer structure characterized as follows:

(A) a polymer having at least one repeating unit selected from the group:

15



20

wherein:

R is selected from  $\text{R}^3$  and  $\text{R}^1\text{NHCOR}^2$ ,

$\text{R}^1$  and  $\text{R}^3$ , individually, are selected from m-phenylene, p-phenylene, 3,3'-biphenylene, 3,4'-biphenylene, 4,4'-biphenylene and 4,4'-diphenylene ether,

25

$\text{R}^2$  is selected from  $\text{R}^1$  and  $-(\text{CH}_2)_x$ ,

Ar is a trisubstituted aromatic radical in which two of the three radical bonds are adjacent to one another and attached to nitrogen atoms, and

30

x is 1 to 10, preferably 1 to 4; said repeating unit further optionally substituted with halogen or  $\text{C}_y\text{H}_{2y+1}$  wherein y is 1 to 10; and

(B) a metal selected from any of Groups 8 through 12 of the Periodic Table of the Elements, chromium, lead and indium; said metal dispersed on the polymer surface and penetrating uniformly into the polymer matrix to a depth of at least 70 nanometers.

35

A second type of metallized polymer of this invention comprises:

5 (A) a polymer having at least one repeating unit as defined above for the first type of metallized polymer;

(B) a first metal selected from Groups 8 through 12 of the Periodic Table of the Elements, chromium, lead and indium, said metal dispersed on  
10 the polymer surface and penetrating uniformly into the polymer matrix to a depth of at least 70 nanometers; and

(C) at least one coating containing one or  
15 more metals selected from Groups 8 through 12 of the Periodic Table of the Elements, chromium, lead and indium, said coating layered over said first metal; and said coating having

(a) an Adherence Factor of at least about  
20 70; and

(b) a Conductivity Value of at least about 70.

The Adherence Factor represents a measure of the degree of adhesion of the coating to the polymer  
25 substrate and the Conductivity Value represents a measure of the uniformity and thickness of the coating on the polymer substrate.

A third type of metallized polymer of the present invention is semiconductor imbibed and is  
30 characterized as follows:

(A) a polymer having at least one repeating unit as defined above for the first type of metallized polymer; and

(B) at least one metal selected from the  
35 group cadmium, cobalt, copper, iron, lead, nickel, germanium, tin, gallium, aluminum or zinc treated with a compound that forms a semiconductor therewith;

said metal penetrating uniformly into the polymer matrix to a depth of at least 70 nanometers.

- 5            Optionally a coating containing one or more metals selected from Groups 8 through 12 of the Periodic Table of the Elements, chromium, lead, and indium can be layered over the semiconductor.

- For each type of metallized polymer the  
10 depicted repeating units, polyamide, polyurea, and polybenzimidazole, respectively, can be substituted with one or more additional substituents that do not interfere with the process as described herein. Preferred among these optional substituents are those  
15 specified, i.e., halogen, most preferably chlorine and bromine, and  $C_yH_{2y+1}$ , wherein y is 1 to 10. Representative of contemplated trisubstituted aromatic radicals is 1,2,4-benzenetriyl.

- The method of this invention for metallizing a  
20 polymer substrate comprises the steps (i), (ii), (iii) and optionally (v); or (i), (ii), (iv) and optionally (v):

- (i) treating a polymer having at least one repeating unit as defined above with a nonaqueous  
25 solution of a strong base to generate anionic sites on the polymer surface,

          (ii) contacting the polymer with metal cation to electrostatically bond the cation to the anionic sites, and

- 30            (iii) reducing the metal cation to metal at the anionic sites on the polymer surface and forming metallic sites, or

- (iv) treating the metal cation generated in step (ii) above with a compound that forms a  
35 semiconductor therewith and forming a semiconductor imbibed polymer; and

          (v) optionally coating the polymer of step (iii) or (iv) with a metal using electroless plating or electrodeposition.

A contemplated variation of the method of this invention comprises mixing the desired polymer  
 5 polyanion solution with the desired metal cation to form a viscous solution, shaping the mixture, reprotonating the polyanion, and reducing the metal cation to metal or treating it as described hereafter to make it semiconductive. In this variation, it is  
 10 most convenient to cast films or fibers of the solution mixture before reduction to the metal or treatment to form a semiconductor.

#### DESCRIPTION OF THE FIGURES

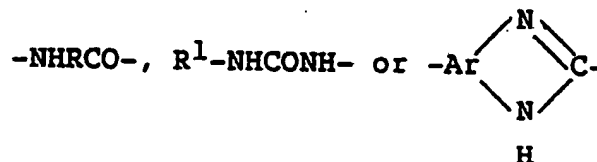
Figure 1 represents an electron micrograph of a  
 15 cross-section of a metallized polymer film treated by the method of U.S. Patent 4,634,805. Scale 1 cm = 170 nm.

Figure 2 represents an electron micrograph of a  
 cross-section of a metal imbibed polymer film treated  
 20 according to steps (i), (ii) and (iii) of the method of the present invention. Scale: 1 cm = 200 nm.

Figure 3 represents an electron micrograph of a  
 cross-section of a metal imbibed and coated polymer  
 film treated according to steps (i), (ii), (iii) and  
 25 (v) of the method of the present invention. Scale: 1 cm = 170 nm.

#### DETAILS OF THE INVENTION

All of the contemplated polymers of this  
 invention have at least one repeating unit selected  
 30 from the group:



35 wherein:

R is selected from  $\text{R}^3$  and  $\text{R}^1\text{NHCOR}^2$ ,  
 $\text{R}^1$  and  $\text{R}^3$ , individually, are selected from  
 m-phenylene, p-phenylene, 3,3'-biphenylene,



3,4'-biphenylene, 4,4'-biphenylene and  
4,4'-diphenylene ether,

5  $R^2$  is selected from  $R^1$  and  $-(CH_2)_x$ ,

Ar is a trisubstituted aromatic radical in  
which two of the three radical bonds are adjacent to  
one another and attached to nitrogen atoms, and

x is 1 to 10, preferably 1 to 4. The depicted  
10 repeating units, polyamide, polyurea, and  
polybenzimidazole, respectively, can be substituted  
with one or more additional substituents that do not  
interfere with the process as described herein.  
Preferred among these optional substituents are  
15 halogen, most preferably chlorine and bromine, and  
 $C_yH_{2y+1}$ , wherein y is 1 to 10. Representative of  
contemplated trisubstituted aromatic radicals is  
1,2,4-benzenetriyl.

When the polymer comprises repeating units of  
20  $R^3$  solely, it can be characterized as a homopolymer.  
Homopolymers are also formed when  $R^1$  and  $R^2$  are the  
same throughout the polymer. Copolymers result when  
 $R^1$  and/or  $R^2$  vary within the polymer matrix.

The polymers of this invention should have a  
25 weight average molecular weight of about 2500 or  
more. Preferred molecular weights are at least about  
3300, indicated by an inherent viscosity of about 0.4  
or greater measured at 0.5% concentration in  
concentrated (95% to 98%) sulfuric acid at 30°C.

30 Contemplated polymers include poly(para-  
phenylene terephthalamide) [PPTA], poly(metaphenylene  
isophthalamide) [PMIA], poly(parabenzamide),  
poly(4,4'-biphenylene isophthalamide), poly(benzimidi-  
zoles), poly(chloroparaphenylene isophthalamide) and  
35 copolymers thereof.

In the method of the present invention,  
typically, the polymer substrate is first treated  
with a solution of a strong base to generate surface

anionic sites. The treated structure is then contacted with a solution of the desired metal cation which is adhered to it via ion exchange. The metal cation is then treated with a compound that forms a semiconductor to yield a semiconductor imbibed polymer or is reduced to the metal state by interaction with the polymer structure to obtain a metal imbibed polymer. If the polymer structure is not of sufficient reduction potential, the cation is reduced by interaction with a solution of a strong reducing agent. Optionally, a second metal is then deposited via electroless plating or electro-deposition to obtain a metal coated polymer.

Strong bases which can be used in the process of the invention include alkali metal hydroxides ( $\text{OH}^-$ );  $\text{R}^4\text{R}^5\text{N}^-$ , wherein  $\text{R}^4$  and  $\text{R}^5$  are selected from the group consisting of  $\text{C}_1\text{-C}_{12}$  alkyl,  $\text{C}_6\text{H}_5$ ,  $\text{C}_{10}\text{H}_7$ ,  $\text{C}_{12}\text{H}_9$ ,  $\text{C}(=\text{O})\text{R}^6$  wherein  $\text{R}^6$  is  $\text{C}_1\text{-C}_{12}$  alkyl;  $\text{CH}_2\text{CN}^-$ ;  $\text{R}^{7-}$  wherein  $\text{R}^7$  is  $\text{C}_1\text{-C}_{12}$  alkyl;  $\text{H}^-$ ;  $\text{R}^8\text{SOR}^9-$  wherein  $\text{R}^8$  and  $\text{R}^9$  are each  $\text{C}_1\text{-C}_{12}$  alkyl or  $\text{R}^{10}\text{O}^-$  wherein  $\text{R}^{10}$  is  $\text{C}_1\text{-C}_{12}$  alkyl; and the polyanions of the polymers described above.

The preferred bases include  $\text{R}^8\text{SOR}^9-$  and  $\text{RO}^-$ . The most preferred bases are  $\text{CH}_2\text{SOCH}_3^-$ , potassium t-butoxide, and the polyanions of the polymers described above either used alone or in the presence of alcohols, amines or nitrates. One preferred mixture of bases is potassium t-butoxide and lithium nitrate. It is advantageous to have more than one alkali metal cation present. The concentration of base in solution can range from .001M to 6M. The most preferred range is 0.1M to 1.0M.

Solvents which are suitable for the invention include sulfoxides such as  $\text{R}^{11}\text{SOR}^{12}$  wherein  $\text{R}^{11}$  and

R<sup>12</sup> can be the same or different and are C<sub>1</sub>-C<sub>5</sub> alkyl. The most preferred solvent is dimethyl-sulfoxide (DMSO).  
5

Solvent and solvent mixtures which are suitable include R<sup>11</sup>SOR<sup>12</sup> and R<sup>11</sup>SOR<sup>12</sup> mixed with a polar non-protic solvent such as N-methylpyrrolidone or tetrahydrofuran. Preferred solvent mixtures contain  
10 greater than 10% DMSO. Most preferred solvent mixtures contain greater than 50% DMSO. It is important to the present invention that the combination of base and solvent cause swelling of the polymers as this permits improved contact with the  
15 reagents. Solvents and solvent combinations which cause swelling are known in the art. See U.S. Patent 4,785,038.

The process of the present invention can be operated at temperatures that vary depending on the  
20 particular solvent that is employed, typically varying between the melting and boiling points of said solvent. For example, when the solvent is DMSO, the temperature range will be 17°C to 190°C. Preferred temperature range is room temperature to  
25 about 60°C. The process can be operated most conveniently at a pressure of subatmospheric to 35,000 psig (2382 atm.).

Metals which can be used for the metallization of the polymer substrate include those in Groups 8  
30 through 12 of the Periodic Table of the Elements plus chromium, lead and indium. Preferred metals include copper, silver, gold, cadmium, zinc, platinum, iron, cobalt, chromium, tin, lead, rhodium, ruthenium, and nickel either individually or as mixtures. Of said  
35 metals, cadmium, cobalt, copper, iron, lead, nickel, germanium, tin, gallium, aluminum and zinc can be

employed to make the semiconductive coating. The concentration of these metal cations in the treating solution should be at least 0.01 M. Typically, the concentration of metal cations is about 0.2 M. Any metal or metal complex can be used that has appropriate solubility in the solvent of choice.

To prepare the semiconductor imbibed polymers of this invention, steps (i), (ii) and (iv) and optionally (v) of the method of this invention are employed. To imbibe the polymer with a semiconductor, the polymer is treated with a strong base to generate anionic sites on its surface and then contacted with an appropriate metal cation as previously described. The metal cation is not reduced but is instead treated with a compound that forms a semiconductor therewith. Various sulfides, selenides or the like known in the art can be employed to produce the semiconductor. This method is especially useful for imbibing a semiconductor in a polymer fiber such as poly(paraphenylene terephthalamide), available from E. I. du Pont de Nemours and Company as Kevlar®.

For the metal imbibed polymers, use of a reducing agent may be necessary with some metals to reduce the cation to the metallic state. Reducing agents suitable for the process of this invention include but are not limited to metal hydrides, hydrazines, electropositive metals, metal complexes, organometallics, borohydrides, boranes and alkylboranes as well as the particular polymer polyanions described herein.

After reduction of the cation to metal or treatment to form a semiconductor, a second metal optionally can be deposited thereon. The additional metal coating can be applied by electrodeposition or by electroless plating techniques. The latter can

be employed to deposit metal on the surface already  
activated by the first metal using steps (i), (ii)  
5 and (iii) or (i), (ii) and (iv) of the method of this  
invention. Materials suitable for use in activation  
include the ions of silver, copper, tin, gold, nickel  
and palladium. Most preferred for use as the  
activating metal is silver or tin. Metals suitable  
10 for the outer coatings include those previously  
listed as suitable for metallization of the polymer  
substrate and include those in Groups 8 through 12 of  
the Periodic Table of the Elements, chromium, lead or  
indium. Use of the optional electroless plating  
15 permits exposure time to the base solution and metal  
cation solution to be minimized, often to only a few  
seconds. The electroless plating yields a coated  
polymer surface that is highly reflective, smooth and  
uniform. For example, a polymer treated with silver  
20 using steps (i), (ii) and (iii) of the method of the  
present invention, followed by electroless plating  
with copper has an electrical resistance nearly as  
low as bulk copper metal.

In all of the polymers of the present  
25 invention, due to the bonding of metal to polymer,  
the metal penetrates uniformly into the polymeric  
matrix, to a depth of at least 70 nanometers.  
Typically, much of the metal will penetrate to a  
depth of about 100 to 500 nanometers. The metallized  
30 polymers of the present invention therefore can be  
distinguished from those prepared by known methods by  
electron microscopy and scanning transmission  
electron microscopy due to this penetration of the  
metal into the polymer matrix. Metallized polymers  
35 prepared by previously known methods typically may  
have metal sporadically distributed through the  
polymer surface layer but lack the uniform

penetration into the polymer matrix. This penetration results from the ion exchange reaction between the anionic sites generated in the polymer matrix swelled by the base/solvent combination and the metal cations. The penetration generates superior adhesion of metal to polymer.

This is demonstrated by the electron micrographs represented in Figures 1, 2 and 3. Figure 1 is a cross-section of a metallized poly(paraphenylene terephthalamide) film prepared by using the prior art method of U.S. Patent 4,634,805 as described in Example 15. The metal appears sporadically distributed on the polymer surface with little or no penetration into the polymer matrix. Figure 2 is a cross-section of a metal imbibed poly(paraphenylene terephthalamide) film treated according to steps (i), (ii) and (iii) of the method of the present invention. The penetration of the silver metal into the polymer matrix can be clearly seen. Figure 3 is a cross-section of a metal coated poly(paraphenylene terephthalamide) film treated according to steps (i), (ii), (iii) and (v) of the method of the present invention resulting in a polymer having copper coated over imbibed silver. The penetration of the silver into the polymer matrix is clearly evident.

For the coated polymers prepared from steps (i), (ii), (iii) and (v) of the method of the present invention, the coating of metal contained on the final product can range from 0.001 to 100 micrometers thick. This type of coated polymer has a more uniform coating of metal to polymer and better adhesion of metal on polymer than previously known coated polymers. The coated polymers prepared by

steps (i), (ii), (iii) and (v) of the method of the present invention have an Adherence Factor of at least about 70. The Adherence Factor is a measure of the degree of adhesion of the coating to the polymer substrate. It is the percentage of coating on a coated sample in film form that does not separate from the substrate when tested in accordance with ASTM D3808-79 (Reapproved 1984) published December, 1979, which is hereby incorporated by reference.

These same coated polymers have a Conductivity Value of at least about 70. This criterion measures the uniformity of the coating on the polymer substrate by determining the electrical conductivity of monofilaments. Areas of discontinuities in the coating or variable coating thickness which can adversely affect the ability of the composition to conduct electricity are minimized or eliminated in the claimed invention. The Conductivity Value is measured as follows. Representative single coated filaments are mounted on a solid support. Silver paste is applied to the filaments at one centimeter intervals to act as conductor leads. Upon application of a voltage to the leads, the presence of conductivity is determined. For polymers of the present invention, at least 7 out of 10, or 70%, of the leads will show conductivity greater than 0.1 reciprocal ohm per meter.

The following Examples illustrate the invention.

#### EXAMPLE 1

Silver-imbibed poly(paraphenylene terephthalamide) [PPTA] yarn was prepared as follows. Six inch lengths of PPTA yarn were washed with water, followed by acetone and methylene chloride and then oven-dried. Sections of yarn were

dipped for five minutes into a solution of 0.5 M potassium t-butoxide in DMSO. This generated an orange gel on the surface of the fibers. The yarn was then placed into a solution of 0.5 M silver trifluoroacetate in DMSO for two minutes. This caused the orange gel to become black. The yarn was next placed in a solution of 0.5 M sodium borohydride in DMSO for two minutes. This caused no further color change, but gas evolution took place from the fiber surface. Finally, the yarn was washed with water, followed by acetone, and then hexane. The yarn sample was then air-dried. A second section of PPTA yarn was similarly treated only with residence times of two minutes in the potassium t-butoxide solution, one minute in the silver trifluoroacetate solution, and two minutes in the sodium borohydride solution. Conductivity measurements showed that both of these samples were electrical conductors.

#### EXAMPLE 2

Copper-imbibed poly(paraphenylene terephthalamide) [PPTA] yarn was prepared as follows. Six inch lengths of PPTA yarn were washed with water, followed by acetone and methylene chloride and then oven dried. Sections of the PPTA yarn were dipped first in a solution of 0.5 M potassium t-butoxide in DMSO for two minutes. Then the yarn was transferred to a solution of 0.5 M cuprous bromide dimethyl sulfide complex in DMSO for two minutes. The yarn was then placed in a solution of 0.5 M sodium borohydride in DMSO for thirty minutes. The resulting copper imbibed yarn was then rinsed liberally with water and vacuum-dried.



EXAMPLE 3

Copper-imbibed poly(paraphenylene  
5 terephthalamide) [PPTA] yarn was prepared as  
follows. PPTA yarn was coated with copper by a  
procedure identical to that of Example 2, except that  
0.5 M of copper bis-trifluoromethanesulfonate benzene  
10 complex in DMSO was used in place of the cuprous  
bromide complex. The resulting copper imbibed yarn  
was electrically conductive.

EXAMPLE 4

Nickel sulfide semiconductor-imbibed  
poly(paraphenylene terephthalamide) [PPTA] films were  
15 prepared as follows. A solution of 0.10 g of nickel  
chloride hydrate in 2 ml of DMSO was added to a  
solution of 74.9 g of a 1.33 weight percent PPTA  
polyanion solution as the potassium salt. A gel  
immediately formed, but vigorous stirring restored a  
20 viscous solution with some small gel particles. The  
resulting solution was used to cast a film which was  
quenched with water to restore the neutral PPTA  
polymer. Treatment of the film with an aqueous  
solution of sodium sulfide gave a PPTA film  
25 containing nickel sulfide particles.

EXAMPLE 5

Semiconductor-imbibed poly(paraphenylene  
terephthalamide) [PPTA] fibers were prepared as  
follows. A solution of 0.10 g nickel acetyl-  
30 acetate in 4 ml of DMSO was added to a solution of  
75.4 g of 1.28 weight percent PPTA polyanion solution  
as the potassium salt. The solution became a gel.  
Addition of 1.32 ml of methanol converted the gel to  
a viscous solution. Fibers were prepared by  
35 extruding this solution from a syringe needle into an  
aqueous quench bath. The fibers were liberally

5 rinsed with water and then with acetone and then dried. The dried fibers were treated with an aqueous solution of sodium sulfide to give PPTA fibers containing nickel sulfide. Elemental analysis showed that the fibers, before sodium sulfide treatment, contained 1.7% nickel.

#### EXAMPLE 6

10 Nickel sulfide semiconductor-imbibed poly(paraphenylene terephthalamide) [PPTA] fibers were prepared as follows. PPTA fibers were dipped into a solution of 0.5 M potassium t-butoxide in DMSO for one minute and then into a solution of 0.08 M  
15 nickel acetyl acetonate for one minute. The fibers were rinsed liberally with THF followed by pentane and then treated with aqueous sodium sulfide, rinsed with water, and dried to give nickel sulfide coated PPTA fibers. Reaction times were also varied: one  
20 minute in the potassium t-butoxide solution and three minutes in the nickel acetyl acetonate solution and also three minutes in the potassium t-butoxide solution and thirty minutes in the nickel acetyl acetonate. In all three cases, elemental analysis  
25 showed that the fibers contained between 1 and 2 weight percent nickel.

#### EXAMPLE 7

Nickel-imbibed poly(paraphenylene terephthalamide) [PPTA] fibers were prepared as  
30 follows. PPTA fibers were immersed in a solution of 0.2 M potassium dimethyl in DMSO for one minute and then for three minutes in a solution of 0.5 M nickel chloride hydrate in DMSO and finally in 0.5 M sodium borohydride in DMSO for three minutes. The resulting  
35 black PPTA fibers were washed liberally with water, then acetone, and then dried. This process gave PPTA fibers imbibed with nickel metal.

EXAMPLE 8

Nickel-coated poly(paraphenylene terephthalamide) [PPTA] film was prepared as follows. A section of PPTA film was immersed momentarily in a 0.1 M solution of potassium t-butoxide in DMSO and then in a 0.1 M solution of silver trifluoroacetate in DMSO. The film was washed liberally with water and dried. Nickel was plated onto this silver-treated film using a traditional method of electroless plating as follows: a section of the film weighing 0.038 g was immersed in a solution of 5.0 g of nickel chloride hydrate and 0.2 g dimethyl amine borane in a mixture of 50 ml of water and 50 ml of dimethyl formamide for one and one-half hours. The film was then rinsed liberally with water and dried in a vacuum oven at 110°C for 2 hours. The resulting nickel imbibed film weighed 0.095 g and was electrically conductive.

EXAMPLE 9

Copper-coated poly(paraphenylene terephthalamide) [PPTA] fibers and films were prepared as follows. PPTA fibers and PPTA films were immersed in a solution of 0.1 M potassium dimethyl in DMSO for several seconds at room temperature and then into a solution of 0.1 M silver trifluoroacetate for several seconds at room temperature. The fibers and films were rinsed with water and dried by means of a vacuum. The fibers and films were then immersed for several seconds into a copper electroless plating bath consisting of 22.7 g of copper sulfate penta-hydrate, 12.5 g of sodium carbonate, 70.0 g of sodium potassium tartrate, and 9.0 g of ethylenediaminetetraacetic acid all in 400 ml of deionized water to which was added a solution of 20.0

g of sodium hydroxide in 100 ml of water and 65 ml of  
a 37% formaldehyde solution. A typical copper  
5 metallized PPTA film prepared in this way had a  
copper layer 0.1 microns in thickness by microscopy  
and with an electrical conductivity of  $1.56 \times 10^5$   
(ohm sec)<sup>-1</sup> by the four point probe method, ASTM  
F390-78 (Reapproved 1984) published June 1978, hereby  
10 incorporated by reference.

#### EXAMPLE 10

Copper-coated poly(paraphenylene  
terephthalamide) [PPTA] paper was prepared as  
follows. A sample of commercial paper comprising a  
15 copolymer of PPTA with poly(metaphenylene  
isophthalamide) [PMIA] was soaked in a DMSO/NMP  
mixture to remove the PMIA. The PPTA was then coated  
heavily with a layer of PPTA polyanion solution and  
rinsed with water to give a PPTA bonded paper with a  
20 smooth, film-like coating of PPTA. The resulting  
paper was then immersed in 0.1 M potassium dimethyl  
solution in DMSO for several seconds at room  
temperature and then in 0.1 M silver trifluoroacetate  
in DMSO and then rinsed with water and dried by means  
25 of a vacuum. The paper was then immersed in a copper  
electroless plating bath for approximately 2 minutes,  
rinsed with water and dried in a vacuum to give a  
copper coated PPTA with an electrical resistance  
approximating that of metallic copper.

30

#### EXAMPLE 11

Copper was electroplated on copper-coated  
poly(paraphenylene terephthalamide) [PPTA] by the  
following method. A section of copper-coated PPTA  
fibers weighing 0.031 g was attached to the negative  
35 terminal of a 6 volt battery, and the fibers were  
immersed in a solution of 30 g of copper sulfate in

300 ml of deionized water. A copper wire was attached to the positive terminal of the battery and immersed into the solution. Electroplating for a total of 25 minutes gave PPTA fibers with a thick coat of copper. The copper uptake was 0.21 g and had an electrical resistance approximating that of bulk copper metal.

10

EXAMPLE 12

Lithium diisopropylamide was used as a base for activation of Kevlar® for silver deposition. 1.07 g lithium diisopropylamide was dissolved in 100 mL of degassed anhydrous DMSO to give a 0.1 M solution. Kevlar-49® 1140 denier yarn was dipped into the solution for approximately two minutes. Then the yarn was dipped into a 0.2 M solution of silver nitrate in DMSO for approximately 30 seconds during which time the fiber became a deep gray color. The yarn was then washed liberally with water, dried, and subsequently plated with copper by means of electroless plating. The fibers showed conductivity consistent with a copper conductor. The adhesion of copper to the fibers was good as evidenced by the fact that adhesive tape did not remove copper from the fibers.

20

25

EXAMPLE 13

Potassium t-butoxide/lithium nitrate mixtures were used as a base for activation of Kevlar® for silver deposition. 3.45 g lithium nitrate and 2.24 g potassium t-butoxide were dissolved in 100 mL DMSO to give a DMSO solution that was 0.5 M in lithium nitrate and 0.2 M in potassium t-butoxide. Kevlar-49® yarn was dipped into the potassium t-butoxide/lithium nitrate solution for 30 seconds and then into a 0.2 M silver nitrate solution in DMSO

30

35

to give deep gray colored yarn. The yarn was washed liberally with water, dried and then electrolessly plated with copper to give yarn with metallic levels of conductivity over at least six foot segments and with excellent copper adhesion as judged by application of adhesive tape.

#### EXAMPLE 14

Silver coated Kevlar® fibers were prepared as follows. A section of Kevlar-49® knit fabric was soaked for approximately ten minutes in a DMSO solution that was 0.4 molar in potassium t-butoxide and 0.7 molar in lithium nitrate. The fabric was then rinsed in DMSO and then soaked in a 0.2 molar solution of anhydrous stannous chloride in DMSO for five minutes. The reaction was then quenched in water, and the Kevlar® was washed liberally in water and finally dried with acetone. The resulting activated Kevlar® was metallized by means of a standard silver electroless plating solution to give silver coated Kevlar® fibers with excellent adhesion of metal to the fibers and with resistance of approximately 2 ohms per square.

#### EXAMPLE 15

The adhesion of a copper layer to poly(paraphenylene terephthalamide) [PPTA] films metallized by the claimed and known prior art methods was tested. The assessment of adhesion was in accordance with ASTM D3808-79 for the qualitative determination of adhesion. A representative sample of PPTA film was metallized by the method of U.S. Patent 4,634,805 which is hereby incorporated by reference. A sample of the film was soaked in an aqueous solution that was 0.1 M in palladium chloride and 0.1 M in HCl for two minutes. The sample was

then soaked for two minutes in an aqueous solution that was 0.1 M in stannous chloride and 0.1 M in HCl. The film was then electrolessly plated with copper. A representative sample of PPTA film was metallized by the present invention as in Example 9. Each were divided into six 1" x 1" squares. Adhesive tape was applied to each of the squares. The tape was then removed from the substrate. The six PPTA samples from the method of the prior art showed poor uniformity, with about 70% of the samples showing the desired copper metallic lustre, the remaining 30% showing a gray black haze suggestive of a poorly formed copper layer. Adhesive tape applied to the six test samples showed that the adhesion was qualitatively good in two of the six squares. In the four samples that showed poor adhesion, the failure occurred at the copper/aramid interface as determined visually. In contrast, the six test squares from the present invention showed a uniform coating of copper with the characteristic lustre and showed qualitatively good adhesion in five of the six test samples.

Kevlar® fibers metallized by the claimed and prior art techniques were also examined for uniformity of the copper coating by determining the electrical conductivity of monofilaments. The Kevlar® fibers metallized by the prior art are the commercially available fibers obtained from Materials Concepts Inc., 666 North Hague Avenue, Columbus, Ohio 43204. Representative single filaments were mounted on a solid support. Silver paste was applied to the filaments at one centimeter intervals to act as conductor leads. Copper coated Kevlar® monofilaments from the prior art showed metallic levels of

electrical conductivity in 3 of 14 one centimeter segments. Copper coated Kevlar® monofilaments  
5 prepared by the present invention showed metallic levels of electrical conductivity in 13 of 18 one centimeter segments.

#### EXAMPLE 16

Poly(paraphenylene terephthalamide) [PPTA]  
10 films metallized with copper by the claimed and previously known methods were subjected to electron microscopy. The prior art method involved treatment of the aramid sequentially with stannous ion solution and palladium ion solution followed by electroless  
15 plating. PPTA was treated according to the present invention in a manner similar to Examples 12 and 13. Upon inspection with electron microscopy both films showed a copper surface layer. The PPTA of the present invention showed a uniform layer of silver  
20 particles impregnating the polymeric matrix in a layer just beneath the copper surface layer. The silver particles were present to a depth of about 100 to 500 nanometers. The PPTA coated using the prior art method showed palladium particles sporadically  
25 distributed through the polymer surface layer with poor penetration into the polymeric matrix. No tin was evident.

30

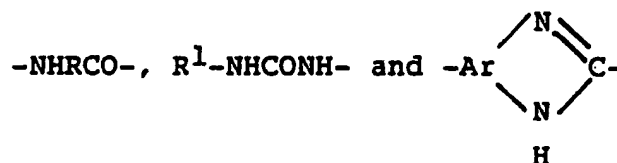
35



I CLAIM:

- 5 1. A method for metallizing polymer substrate with a metal, comprising the steps (i), (ii) and (iii) or (i), (ii), and (iv):
- (i) treating a polymer having at least one repeating unit selected from the group:

10



15

wherein:

R is selected from  $\text{R}^3$  and  $\text{R}^1\text{NHCOR}^2$ ,

$\text{R}^1$  and  $\text{R}^3$ , individually, are selected from m-phenylene; p-phenylene, 3,3'-biphenylene, 3,4'-biphenylene, 4,4'-biphenylene and 4,4'-diphenylene ether,

20

 $\text{R}^2$  is selected from  $\text{R}^1$  and  $(\text{CH}_2)_x$ ,

Ar is a trisubstituted aromatic radical in which two of the three aryl bonds are adjacent to one another and attached to nitrogen atoms, and

25

x is 1 to 10;

with a nonaqueous solution of strong base to generate anionic sites on the polymer surface,

30

(ii) contacting the polymer with a metal cation to electrostatically bond the cation to the anionic sites, and

(iii) reducing the metal cation to metal at the anionic sites on the polymer surface and forming metallic sites, or

35

(iv) treating the metal cation with a compound that forms a semiconductor therewith and forming a semiconductor imbibed polymer.

2. A method according to Claim 1 further  
5 comprising step (v) of coating the polymer of either  
step (iii) or step (iv) with a metal using  
electroless plating or electrodeposition.

3. A method according to Claim 1 wherein x  
10 is 1 to 4 and the repeating unit of the polymer is  
further substituted with one or more members selected  
from the group halogen and  $C_yH_{2y+1}$  where y is 1 to 10.

4. A method according to Claim 3 wherein the  
15 polymer is selected from the group poly(para-  
phenylene terephthalamide), poly(metaphenylene  
isophthalamide), poly(parabenzamide), poly(4,4'-  
biphenylene isophthalamide), poly(benzamidizoles),  
poly(chloroparaphenylene isophthalamide) and  
20 copolymers thereof.

5. A method according to Claim 1 wherein the  
base is selected from alkali metal hydroxides;  
 $R^4R^5N^-$ , wherein  $R^4$  and  $R^5$  is selected from the group  
25 consisting of  $C_1-C_{12}$  alkyl,  $C_6H_5$ ,  $C_{10}H_7$ ,  $C_{12}H_9$ ,  
 $C(=O)R^6$  wherein  $R^6$  is  $C_1-C_{12}$  alkyl;  $CH_2CN^-$ ;  $R^7^-$   
wherein  $R^7$  is  $C_1-C_{12}$  alkyl;  $H^-$ ;  $R^8SOR^9^-$  wherein  $R^8$   
and  $R^9$  are each  $C_1-C_{12}$  alkyl,  $R^{10}O^-$  wherein  $R^{10}$  is  
 $C_1-C_{12}$  alkyl, and the polyanions of the polymers, or  
30 a combination thereof, alone or in the presence of  
alcohols, amines or nitrates.

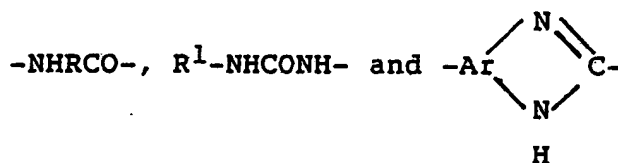
6. A method according to Claim 1 wherein the  
solvent is  $R^{11}SOR^{12}$  wherein  $R^{11}$  and  $R^{12} = C_1-C_5$  alkyl.  
35

7. A method according to Claim 1 wherein the polymer is poly(paraphenylene terephthalamide), the  
 5 base is a mixture of potassium t-butoxide and lithium nitrate and the solvent is dimethylsulfoxide.

8. A method according to Claim 2 or 4 comprising steps (i), (ii) and (iii) or steps (i),  
 10 (ii), (iii) and (v) wherein the metal cation is selected from cations of the group copper, silver, gold, cadmium, zinc, platinum, iron, cobalt, chromium, tin, lead, rhodium, ruthenium, indium and nickel.

15 9. A method according to Claim 2 or 4 comprising steps (i), (ii) and (iv) or steps (i), (ii), (iv) and (v) wherein the metal cation is selected from cations of the group cadmium, cobalt, copper, iron, lead, nickel, germanium, tin, gallium, aluminum and zinc.

10. A metallized polymer structure comprising:  
 (A) a polymer having at least one repeating  
 25 unit selected from the group:



30

wherein:

R is selected from  $R^3$  and  $R^1\text{NHCOR}^2$ ,  
 $R^1$  and  $R^3$ , individually, are selected from  
 35 m-phenylene, p-phenylene, 3,3'-biphenylene, 3,4-biphenylene, 4,4'-biphenylene and 4,4'-diphenylene ether,

$R^2$  is selected from  $R^1$  and  $-(CH_2)_x$ ,

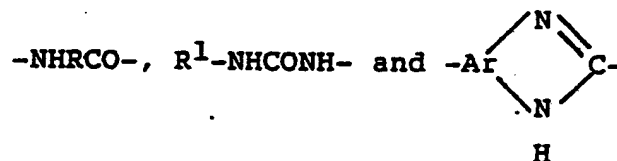
Ar is a trisubstituted aromatic radical in  
 5 which two of the three aryl bonds are adjacent to one  
 another and attached to nitrogen atoms, and

$x$  is 1 to 10; and

(B) a metal selected from any of Groups 8  
 through 12 of the Periodic Table of the Elements,  
 10 chromium, lead and indium, said metal dispersed on  
 the polymer surface and penetrating into the polymer  
 matrix to a depth of at least 70 nanometers.

11. A metallized polymer structure comprising:

15 (A) a polymer having at least one repeating  
 unit selected from the group:



wherein:

$R$  is selected from  $R^3$  and  $R^1NHCOR^2$ ,

25  $R^1$  and  $R^3$ , individually, are selected from  
 m-phenylene, p-phenylene, 3,3'-biphenylene,  
 3,4-biphenylene, 4,4'-biphenylene and  
 4,4'-diphenylene ether,

$R^2$  is selected from  $R^1$  and  $-(CH_2)_x$ ,

30 Ar is a trisubstituted aromatic radical in  
 which two of the three aryl bonds are adjacent to one  
 another and attached to nitrogen atoms, and

$x$  is 1 to 10;

(B) a first metal selected from any of  
 35 Groups 8 through 12 of the Periodic Table of the  
 Elements, chromium, lead and indium, said metal

dispersed on the polymer surface and penetrating into the polymer matrix to a depth of at least 70  
 5 nanometers; and

(C) at least one coating containing one or more metals selected from Groups 8 through 12 of the Periodic Table of the Elements, chromium, lead and indium, said coating layered over said first metal,  
 10 and said coating having

(a) an Adherence Factor of at least about 70; and

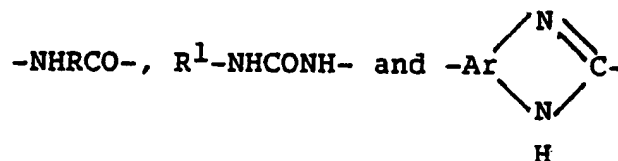
(b) a Conductivity Value of at least about 70.

15

12. A semiconductor imbibed polymer structure comprising:

(A) a polymer having at least one repeating unit selected from the group:

20



25

wherein:

R is selected from  $\text{R}^3$  and  $\text{R}^1\text{NHCOR}^2$ ,

$\text{R}^1$  and  $\text{R}^3$ , individually, are selected from m-phenylene, p-phenylene, 3,3'-biphenylene,  
 30 3,4-biphenylene, 4,4'-biphenylene and 4,4'-diphenylene ether,

$\text{R}^2$  is selected from  $\text{R}^1$  and  $-(\text{CH}_2)_x-$ ,

Ar is a trisubstituted aromatic radical in which two of the three aryl bonds are adjacent to one  
 35 another and attached to nitrogen atoms, and  
 x is 1 to 10; and

(B) at least one metal selected from the group copper, cadmium, zinc, iron, cobalt, lead,  
5 nickel, germanium, tin, gallium, aluminum or zinc treated with a compound that forms a semiconductor therewith; said metal penetrating into the polymer matrix to a depth of at least 70 nanometers.

10 13. The polymer of Claim 10 or 12 wherein the metal is selected from the group copper, silver, gold, cadmium, zinc, platinum, iron, cobalt, chromium, tin, lead, rhodium, ruthenium, indium and nickel.

15 14. The polymer of Claim 13 wherein the metal is selected from silver or copper.

20 15. The metallized polymer of Claim 11 wherein the first metal is selected from the group silver, copper, tin, gold, nickel or palladium and the metal coated onto the first is selected from the group copper, silver, gold, cadmium, zinc, platinum, iron, cobalt, chromium, tin, lead, rhodium,  
25 ruthenium, indium and nickel.

16. The metallized polymer of Claim 15 wherein copper is coated over silver.

30 17. The polymer of Claim 10, 11 or 12 wherein  $x$  is 1 to 4 and the repeating unit of the polymer is further substituted with one or more members selected from the group halogen and  $C_yH_{2y+1}$  wherein  $y$  is 1 to 10.

35

18. The polymer of Claim 10, 11 or 12 wherein  
5 the polymer is selected from the group poly(para-  
phenylene terephthalamide), poly(methaphenylene  
isophthalamide), poly(parabenzamide), poly(4,4'-  
biphenylene isophthalamide), poly(benzamidizoles),  
poly(chloroparaphenylene isophthalamide) and  
10 copolymers thereof.

19. The polymer of Claim 13 or 14 wherein the  
polymer is poly(paraphenylene terephthalamide).

15 20. The polymer of Claim 12 wherein the  
compound that forms a semiconductor with the metal is  
selected from a sulfide or selenide.

21. The polymer of Claim 20 wherein the  
20 semiconductor contains nickel sulfide.

22. The polymer of Claim 12 further  
comprising at least one coating containing one or  
more metals selected from Groups 8 through 12 of the  
25 Periodic Table of the Elements, chromium, lead and  
indium, said coating layered over the semiconductor.

30

35

1 / 3

FIG. 1



SUBSTITUTE SHEET



2 / 3

FIG. 2



SUBSTITUTE SHEET

3 / 3

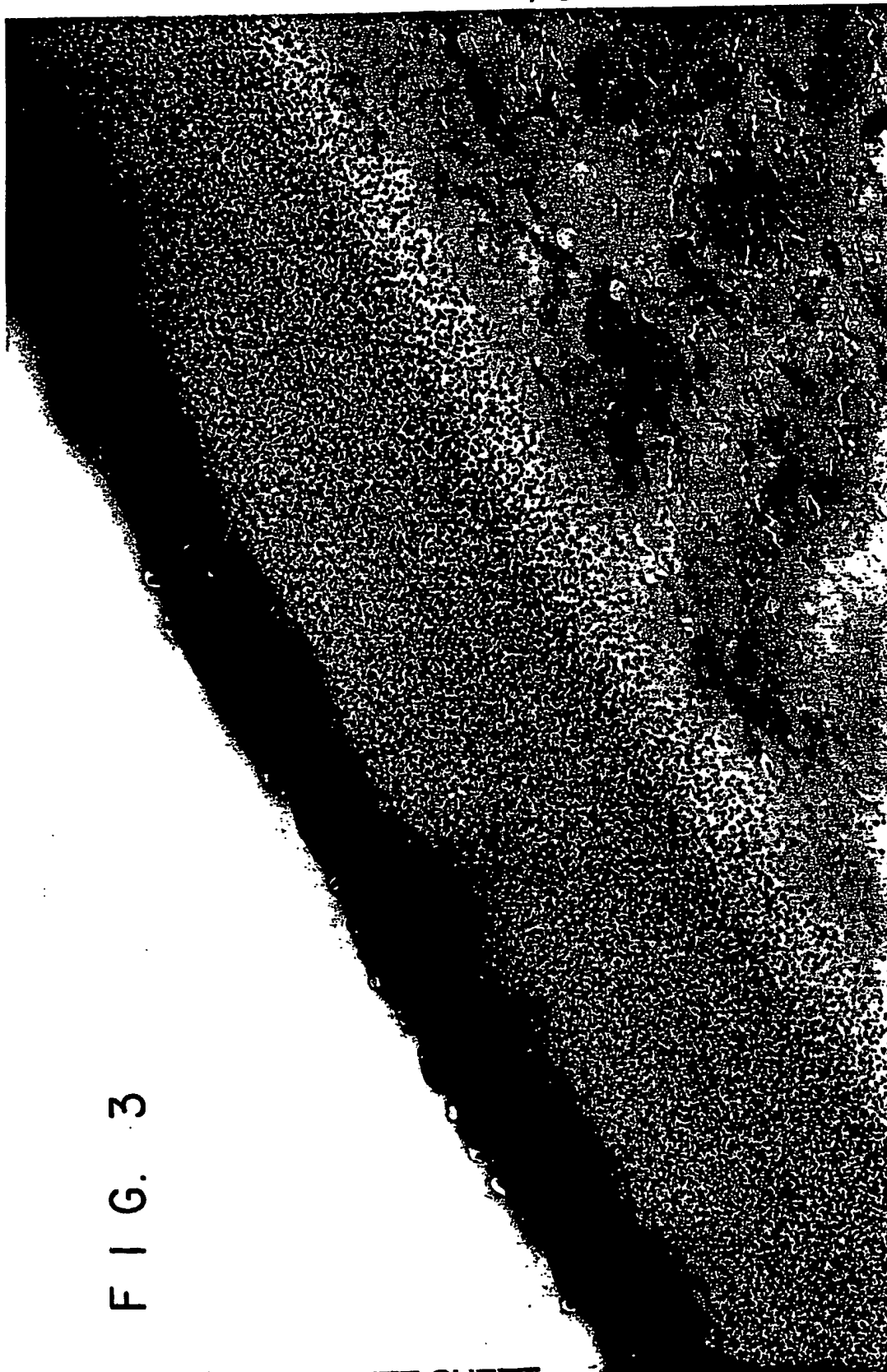


FIG. 3

SUBSTITUTE SHEET

This Page is inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images  
problems checked, please do not report the  
problems to the IFW Image Problem Mailbox**